

ORGANIC MOLECULES IN THE SHEEPBED MUDSTONE, GALE CRATER, MARS. C. Freissinet^{1,2}, D. P. Glavin¹, P. R. Mahaffy¹, K. E. Miller³, J. L. Eigenbrode¹, R. E. Summons³, A. E. Brunner¹, A. Buch⁵, C. Szopa⁶, P. D. Archer⁷, H. B. Franz¹, A. Steele⁶ *et al.*
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Introduction: The Sample Analysis at Mars (SAM) instrument on the Curiosity rover is designed to determine the inventory of organic and inorganic volatiles thermally released from solid samples using a combination of evolved gas analysis (EGA), gas chromatography mass spectrometry (GCMS), and tunable laser spectroscopy [1]. Here we report on various chlorinated hydrocarbons (chloromethanes, chlorobenzene and dichloroalkanes) detected at elevated levels above instrument background at the Cumberland (CB) drill site, and discuss their possible sources.

SAM solid sample analyses: The analyses of gases released from the Rocknest (RN), John Klein (JK), and CB solid samples were conducted by heating the sample portions in a pyrolysis oven to > 800 °C, at a rate of 35 °C/min under 1 standard cubic centimeters per min He flow and 1) monitoring the evolved gases with a quadrupole mass spectrometer (Evolved Gas Analysis, EGA mode), and 2) trapping a specific temperature range of evolved gases using hydrocarbon traps containing Tenax TA and GR and then heating the traps to send the gases through one of the six gas chromatographic columns before analysis in GCMS. Prior to EGA and GCMS analyses of the first 3 solid samples (RN, JK and CB) collected by MSL and delivered to SAM, procedural blank runs were carried out with an empty quartz cup to characterize the volatile sources/background internal to the SAM instrument.

Discussion:

SAM internal sources: The hydrocarbon trap(s) Tenax products are a major part of the SAM internal background measured by GCMS. Other major contributors to the background signal are the reaction products of one of the chemicals used for SAM wet chemistry experiment: *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA) [2]. MTBSTFA fluid was sealed inside each of the seven derivatization cups present in the sample manipulating system. Any MTBSTFA released from the cups will readily react with water present inside the instrument to form by-products, identified in the GCMS blanks by their mass

spectra and used to estimate the initial amount of MTBSTFA present in the sample. The presence of MTBSTFA and other reactive species in the background can create newly formed products by interaction with inorganic species in the martian regolith, such as oxychlorine compounds [3]. Before confirming detection of martian molecules, the possibility that these compounds could be derived from reactions between martian volatiles and terrestrial components internal to SAM has to be eliminated. For this reason, the empty cup blank runs on Mars are required, as are the laboratory experiments performed under SAM-like conditions to understand the reaction products of molecules in the background with known inorganic species in the martian regolith [4,5,6].

Chlorinated hydrocarbons: Chlorobenzene (150-325 parts per billion by weight (ppbw)) and C2 to C4 dichloroalkanes (up to 70 ppbw) have been identified with the SAM GCMS, in multiple portions of the fines from the Cumberland drill hole in the Sheepbed mudstone at Yellowknife Bay (Fig. 1). When combined with data from multiple scooped and drilled samples, blank runs and supporting laboratory analog studies, the elevated levels of chlorobenzene and the dichloroalkanes are inconsistent with the terrestrial volatile background sources known to be present in SAM.

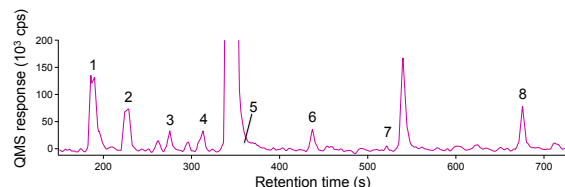


Fig. 1: Gas chromatogram of the CB-3 sample. 1: chloromethane, 2: dichloromethane, 3: trichloromethane, 4: carbon tetrachloride, 5: dichloroethane, 6: dichloropropane, 7: dichlorobutane, 8: chlorobenzene

Chlorobenzene was identified by both retention time and mass spectra in the CB-3, CB-5, and CB-6 runs at levels above background by the SAM GCMS

(Fig. 1). Trace levels (< 10 pmol) of chlorobenzene observed in RN, the CB blank, and in the high temperature cuts used for CB-1 and CB-2 are attributed to reactions between HCl and the Tenax polymer used in the hydrocarbon trap. Much higher levels (90 to 180 pmol) of chlorobenzene were observed in the CB-3, CB-5, and CB-6 GCMS runs that analyzed a lower temperature hydrocarbon trap cut. The CB-6 triple portion run had ~ 2 to 3 times more chlorobenzene than the CB-3 and CB-5 single portion runs. The chlorobenzene level dropped in a second heating of the CB-6 residue. In the CB-5 EGA, several mass fragments released in the 200-350 $^{\circ}\text{C}$ range, including m/z 112 and 114 that can be attributed to chlorobenzene, were not observed above background levels in RN, the empty cup blanks, or the second heating of the CB-6 triple portion residue (Fig 2).

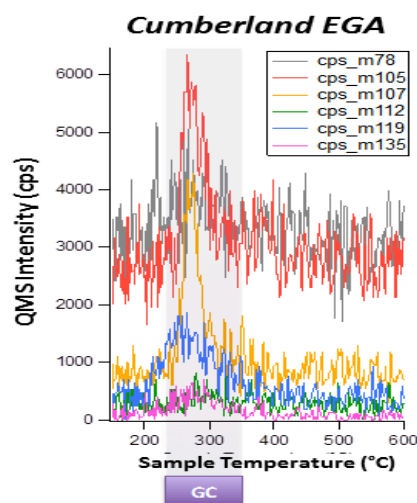


Fig. 2: SAM EGA analysis showing masses corresponding to possible martian hydrocarbon fragments released from CB-5 as a function of sample temperature and the temperature cut indicated by the purple bar sent to the GC.

1,2-Dichloropropane (1,2-DCP), as well as 1,1- and 1,2-dichlorobutane and possibly 1,2-dichloroethane have all been identified in the CB-3 and CB-5 runs. Given the significant reduction of volatiles present in the instrument background in the CB-5 run compared to CB-3 and the lack of these chlorinated alkanes in any of the RN runs, in the blank run or in the reheated CB-6-residue, a martian carbon source for 1,2-DCP in CB is possible. The fact that no 1,2-DCP and none of the dichlorobutane isomers are detected in the laboratory pyrolysis GCMS experiments with MTBSTFA and perchlorates, and that no C3- or C4-alkanes have been detected in similar experiments, suggests that neither MTBSTFA nor the hydrocarbon trap components are a major carbon contributor to these chlorohy-

drocarbons detected in CB. The tentative identification of propane in the CB-5 GCMS analysis, made difficult by its low retention time and weak mass spectrum, indicates that aliphatic hydrocarbons may be available as precursors for the 1,2-DCP detected at CB. This propane could be a fragment of a larger hydrocarbon in the CB sample itself. Laboratory experiments using SAM-like conditions show that 1,2-DCP can be formed from C3-hydrocarbons or C3-alcohols when heated in the presence of perchlorates. In addition, 1,2-DCP is a product of the pyrolysis of the Murchison meteorite organic material in the presence of perchlorates [5].

Conclusion: Taken together, these results indicate that the internal SAM sources create a background that challenges the definitive identification of a martian source of organic carbon for some compounds, creating interferences between terrestrial and possible indigenous carbon sources. However, both laboratory and SAM observations suggest no direct link between SAM internal sources and the elevated levels of dichloropropane and chlorobenzene detected in the Cumberland drilled samples compared to Rocknest, thus a martian organic contribution to the chloromethanes, dichloroalkanes and chlorobenzene detected at CB is being systematically explored.

References: [1] Mahaffy, P. *et al.* (2012) *Space Sci Rev*, 170, 401-478. [2] Buch, A. *et al.* (2014) *LPSC XLV*. [3] Glavin *et al.* (2013) *JGR*, 118, 1-19. [4] Glavin, D. *et al.* (2014), *LPSC XLV*. [5] Miller, K. E. *et al.* (2014), *LPSC XLV*. [6] Miller, K. *et al.* (2013) *AGU XLVI*, #1785